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THEORY OF AFTER-EFFECTS

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THE THERMODYNAMICAL THEORY OF THE RELAXATION PHENOMENA AND ITS CONNECTION
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by J. Meixner

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1. Definition of the problem.

There are two general theories of the linear relaxation phenomena that make it possible to describe the relaxation phenomena without getting involved in the molecular mechanisms. One of them is the thermodynamic theory which assumes the existence of internal transformations only, without requiring any more detailed specifications thereof. Their basis is the thermodynamics of the irreversible processes; for that reason, it is able consistently to take into consideration not only the various conditions under which a relaxation process can take place adiabatically or isothermically, with constant pressure or constant volume, with constant electric field intensity or constant electrical shift density, etc. - but also to establish connections between the relaxation times or relaxation spectra that are valid for the various conditions. The theory of the after-effect of the relaxation phenomena is still more general and, thereby, at the same time more formal than the thermodynamic theory; it is essentially based on two theorems: 1. The effect cannot precede the cause, 2. The superposition principle applies to several independent causes and their effects. This great generality of the conditions makes it impossible any longer to arrive at conclusions regarding the connection of the relaxation processes that take their course under different conditions. Beyond this, its formalism comprises processes that are

not contained any longer in the thermodynamic theory.

Besides this theory, we also have a kinetic theory of the relaxation phenomena (Kronig (1)); but it is so closely related to the thermodynamic theory that we shall not have to make any distinction between them, within the framework of the following considerations.

It is the purpose of the following explanations to clarify the thermodynamic theory of the relaxation phenomena for one internal mechanism as well as for a finite and infinite number of such mechanisms, to indicate a series of general laws, and to discuss the dynamic equations of state that will come into existence by the elimination of the internal parameters. From this point, there is a direct bridge leading to the after-effect theory of the relaxation phenomena, which also enables us to see precisely, where the equivalence of the two theories ends. Starting from this point, we shall be able to look for a way leading to a generalization of the thermodynamics of irreversible processes that is equivalent to the formalism of the theory of after-effects in a more comprehensive area, and that renders it precise.

By way of complementation, we shall point out an example of the dielectric relaxation and the connection between the thermodynamic relaxation theory of a system having an infinite number of internal transformations and its linearized basic kinetic equation.

In all our considerations, we shall assume that the deviations from the thermodynamic equilibrium will always be sufficiently small; that means, on the one hand, that the thermodynamics of the irreversible processes are applicable, and on the other hand, that the superposition principle is valid. We shall then - as we already have done at the outset - speak of linear relaxation phenomena. Moreover, we shall consider here only homogeneous systems

and their reaction to outside effects, but without any pronounced transport phenomena. Even though the considerations and results will be presented in the language of mechanical relaxation, they can nevertheless be applied analogously to all other relaxation phenomena provided they have been translated correctly.

2. Thermodynamic systems having one internal transformation.

We shall consider a system within which one internal transformation is possible; this transformation may be, e.g., a chemical reaction in the true meaning of the term, a transition between various states of a molecule, or an internal rearrangement. The thermodynamic state of this system will then be described, perhaps, by the indication of the temperature T , of the specific volume and of an internal variable ξ . This variable may be, e.g., the variable number of the reaction of the internal transformation or the concentration of a component taking part in the transformation or the internal temperature T_1 , in the usual sense. In the case of a thermodynamic equilibrium, ξ depends on T and v ; we shall then write that $\xi = \bar{\xi}(T, v)$. When ξ represents the internal temperature of T_1 , then the condition of equilibrium will simply be $T_1 = T$. It is possible also to choose other pairs of variables instead of T and v ; e.g., T , p or s , v , or s , p , where s denotes the entropy and p denotes the pressure.

The reaction velocity $d\xi/dt$ may be considered - at least, in the case of the small deviations from the equilibrium, that we shall have to consider here - a function of the state prevailing at the time t ; then, we shall be able to write (2)

$$\frac{d\xi}{dt} = \varepsilon(T, v, \xi) \cdot A(T, v, \xi). \quad [1]$$

$A(T, v, \xi)$ is the affinity as understood in the meaning of de Donder, in the state T, v, ξ , and as defined by Gibbs' equation for the differential of the specific energy, viz,

$$du = Tds - pdv - Ad\xi; \quad [2]$$

it is, therefore, the conjugated value for ξ . In the equilibrium, the affinity will disappear; according to [1], $d\xi/dt$ will also disappear, at the same time - of necessity. Otherwise, the transformation velocity will be determined by the coefficient $\epsilon(T, v, \xi)$. Since we shall limit ourselves to small deviations from the equilibrium, it will be sufficient, to substitute the value of the equilibrium, $\bar{\xi}(T, v)$ for ξ in $\xi(T, v)$, i. e., to consider ϵ solely as a function of T and v or, when we select other independent variables s, v , as a function of s and v , etc. In doing so, we shall neglect the terms in [1] that are proportionate to A^2 .

Very small catalyzing or de-catalyzing additions to our system will practically leave its thermodynamic properties unaffected; but, they may have a considerable effect on the transformation velocity. For that reason, they will be taken into account simply by assuming that ϵ will depend also on their quantity.

The velocity at which a disturbance of the equilibrium dies down, is given by [1]; it depends on the conditions of the relaxation process. When, e.g., T and v are retained then it will follow from [1], by developing for powers of $\xi - \bar{\xi}(T, v)$ due to $A(T, v, \bar{\xi}(T, v)) = 0$ that there will be

$$\frac{d\xi}{dt} = \epsilon \left(\frac{\partial A}{\partial \xi} \right)_{T, v} [\xi - \bar{\xi}(T, v)] \quad [3]$$

in the first approximation. It follows therefrom, by integration, since $\bar{\xi}(T, v)$ is constant that

$$\xi(t) = \bar{\xi}(T, v) + C \cdot e^{-t/\tau_{Tv}} \quad [4]$$

when

$$\tau_{Tv} = -\frac{1}{\varepsilon} \left(\frac{\partial \xi}{\partial A} \right)_{T,v}. \quad [5]$$

C is an integration constant, the value of which indicates the initial deviation from the equilibrium; τ_{Tv} is the relaxation time, when T and v are constant.

On the other hand, when s and v are constant during the relaxation process, then we shall find it helpful to select s and v as independent variables; we shall then obtain from [1], by analogy,

$$\frac{d\xi}{dt} = \varepsilon \left(\frac{\partial A}{\partial \xi} \right)_{s,v} [\xi - \bar{\xi}(s,v)]. \quad [6]$$

Now, $\bar{\xi}(s,v)$ will be constant (but not $\bar{\xi}(T,v)$, since the temperature may change under the condition of constant entropy which is present in this case), and it follows, with an integration constant C, that

$$\xi(t) = \bar{\xi}(s,v) + C \cdot e^{-t/\tau_{sv}}, \quad [7]$$

when now

$$\tau_{sv} = -\frac{1}{\varepsilon} \left(\frac{\partial \xi}{\partial A} \right)_{s,v} \quad [8]$$

will be the relaxation time when s and v are constant. The relation of these two relaxation times will not contain the value of s that determines the velocity, and is therefore a purely thermodynamic value. The inequality (2)

$$\tau_{sv} \leq \tau_{Tv}. \quad [9]$$

will follow from general thermodynamic considerations. The sign of equality will be valid only when $(\partial \xi / \partial A)_{s,v} = (\partial \xi / \partial A)_{T,v}$, and thereby $(\partial \xi / \partial T)_{A,v} = 0$; i.e., when the position of the equilibrium does not depend on the temperature, while the volume is being retained.

In an analogous manner, we shall define the relaxation times τ_{sp} , τ_{Tp} for the relaxation when s, p or T, are constant; we shall then obtain the inequalities

$$\tau_{sv} \leq \tau_{Tv} \leq \tau_{Tp}; \quad \tau_{sv} \leq \tau_{sp} \leq \tau_{Tp}, \quad [10]$$

which - just as [9] - are closely linked with the principle of le Chatelier-Braun. Then and only then

$$\tau_{sv} = \tau_{Tv} \quad \text{when} \quad \left(\frac{\partial \xi}{\partial T} \right)_{v, A} = 0,$$

$$\tau_{sv} = \tau_{sp} \quad \text{when} \quad \left(\frac{\partial \xi}{\partial v} \right)_{s, A} = 0,$$

$$\tau_{sp} = \tau_{Tp} \quad \text{when} \quad \left(\frac{\partial \xi}{\partial T} \right)_{p, A} = 0,$$

$$\tau_{Tv} = \tau_{Tp} \quad \text{when} \quad \left(\frac{\partial \xi}{\partial v} \right)_{T, A} = 0,$$

$$\tau_{sv} = \tau_{Tv} = \tau_{sp} = \tau_{Tp} \quad \text{when } \xi \text{ is not dependent on } T \text{ and } v \text{ in the state of equilibrium.}$$

We shall attempt, by using the case of [9], to render these inequalities clearly evident. We shall consider a molecular gas with a translational and rotational temperature of T. We shall assume that the occupation of the first excited level of oscillation (which is the only one being considered here) is larger than it would be in accordance with the Boltzman factor for the temperature T. We shall select as the internal parameter ξ , and internal temperature $T_1 > T$, which is defined as the system temperature, at which the assumed occupation of the level of oscillation would be in a state of thermodynamic equilibrium with translation and rotation. When T, v are constant, the relaxation process will require a cooling from the initial value T_1 of the internal temperature down to T. But, when we retain s and v, then T will increase during the relaxation process (transmission of energy from the degree of freedom of the oscillation into the degrees of freedom of the translation and

rotation); this means that the relaxation process signifies an adjustment from the initial value of T to a higher terminal value, and a smaller decrease of the internal temperature than when T, v are fixed, and that - accordingly - it will be "terminated" more rapidly.

3. The dynamic equation of state.

While we have considered the Equation [1], up to this point, only for those conditions, under which two independent variables will be retained, we shall now assume at random time dependence for two independent variables, but with the restriction that no large deviations from a fixed state of reference of T_0, v_0, ξ_0 with $\xi_0 = \xi(T_0, v_0)$ will occur. We shall use - besides [1] - the equation of state

$$p = p(T, v, \xi) \quad [11]$$

which we shall use also in the form of $p = p(s, v, \xi)$ etc., depending on our requirements. Since we have assumed that two of the independent variables are known, [1] and [11] may be used to find the other values, viz. p, T, v, ξ . When we eliminate ξ , a relation between p, T, v and their time derivations will remain; we shall call it the dynamic equation of state in a differential form.

In the environs of the state of reference T_0, v_0, ξ_0 [1] and [11] will read as follows when we neglect the higher terms of the development:

$$\frac{1}{\epsilon} \frac{d}{dt} (\xi - \xi_0) = \left(\frac{\partial A}{\partial T} \right)_{v, \xi} (T - T_0) + \left(\frac{\partial A}{\partial v} \right)_{T, \xi} (v - v_0) + \left(\frac{\partial A}{\partial \xi} \right)_{T, v} (\xi - \xi_0), \quad [12]$$

$$p - p_0 = \left(\frac{\partial p}{\partial T} \right)_{v, \xi} (T - T_0) + \left(\frac{\partial p}{\partial v} \right)_{T, \xi} (v - v_0) + \left(\frac{\partial p}{\partial \xi} \right)_{T, v} (\xi - \xi_0) \quad [13]$$

when $p_0 = p(T_0, v_0, \xi_0)$. All partial derivations will have to be made for the state of reference. On the basis of simple transformations, the eliminations of $\xi - \xi_0$ will result in

$$p - p_0 + \tau_{pv} \dot{p} = \left(\frac{\partial p}{\partial T} \right)_{v, A} [T - T_0 + \tau_{pv} \dot{T}] + \left(\frac{\partial p}{\partial v} \right)_{T, A} [v - v_0 + \tau_{Tp} \dot{v}]. \quad [14]$$

Here, τ_{pv} appears as the new relaxation time; it is defined, in a manner

analogous to [5] and [8], by

$$\tau_{pv} = -\frac{1}{\varepsilon} \left(\frac{\partial \xi}{\partial A} \right)_{p,v} \quad [15]$$

and refers to the temperature relaxation when p, v are constant.

When we assume that the pressure in the equation of state [11] is a function of s, v , then we shall find, in an analogous manner and in equivalence with [14] that

$$p - p_0 + \tau_{sv} \dot{p} = \left(\frac{\partial p}{\partial s} \right)_{v,A} [s - s_0 + \tau_{pv} \dot{s}] + \left(\frac{\partial p}{\partial v} \right)_{s,A} [v - v_0 + \tau_{s,p} \dot{v}]. \quad [16]$$

Depending on the conditions present, [14] or [16] may be convenient. For adiabatic conditions of $s = s_0$, $\dot{s} = 0$ [15] will be reduced to the well-known acoustical equation of state.

When the changes of state are taking place very slowly, then the time derivations of [14] and [16] may be disregarded, and we shall then come back to the static equation of state. When the changes of state are taking place very rapidly, then we shall be able to disregard - on the other hand - $p - p_0$, $T - T_0$ (or $s - s_0$) and $v - v_0$; the integration for the time will then result - when we take [5], [8] and [16] into account - in

$$p - p_0 = \left(\frac{\partial p}{\partial T} \right)_{v,\xi} (T - T_0) + \left(\frac{\partial p}{\partial v} \right)_{T,\xi} (v - v_0)$$

and in a corresponding equation with s or s_0 in the place of T or T_0 . This relation will have, once more, the form of a static equation of state, but now for the case of a constant ξ . This may be seen directly, since the transformation can no longer follow when the changes of state are sufficiently rapid, i.e., ξ will then remain constant.

The special case of $\tau_{Tv} = \tau_{Tp}$ (and, analogously, the special case of $\tau_{sv} = \tau_{sp}$) is noteworthy. In that case - provided we disregard a trivial exception (viz., when in the environs of the state of reference s depends

solely on T , p depends solely on v , and A depends solely on ξ) we shall find that $\tau_{Tp} = \tau_{pv}$, and we shall then be able to integrate [14] directly, with the result of

$$p - p_0 = A e^{-\tau_{Tp} T} + \left(\frac{\partial p}{\partial T} \right)_{v,A} (T - T_0) + \left(\frac{\partial p}{\partial v} \right)_{T,A} (v - v_0).$$

This is exactly the static equation of state $p = p(T, v)$ when we disregard a term that decreases exponentially, and the coefficient A of which is, in any case, equal to zero when the prescribed change of state $T(t)$, $v(t)$ starts from a state of equilibrium. In that case, the internal transformation will not come to the fore in the relation between p , T , and v . Such a system, that will, therefore, not present any relaxation of the pressure in the case of isothermic changes of state, when the volume is modified, but it may possess such a relaxation under adiabatic conditions, and vice versa; for, the condition of $\tau_{Tv} = \tau_{Tp}$ which is necessary to that end, generally does not entail the condition that $\tau_{sv} = \tau_{sp}$. For that reason, an internal transformation may or may not manifest itself by a relaxation between p and v , depending on the conditions that are present.

An example is the aforementioned relaxation of the heat of oscillation in gases, which is based on the equilibrium adjustment of the level of oscillation of the molecules. Since the mol number remains preserved during this process, the equation of state will read $p v = n R T$ (n = total mol number in gram); accordingly, it does not contain the numbers of electrons occupying the shell, i.e., the internal variable. For that reason, the product $p v$ will remain constant in the case of isothermic changes, while the dynamic equation of state will be reduced - when T is constant - to the static one, despite the possibility of an occurrence of internal transformations. This will apply even when we shall have to take into consideration

not only an internal transformation but all transitions between the levels of rotation and oscillation of the molecules. But, in the case of adiabatic changes of state, the equation of state is a truly dynamic one. This follows not only from the thermodynamics of such a system but also from the observation of the absorption and dispersion of sound waves.

Now we shall compare the differential form of the dynamic equation of state [14] or [16] with an integral form, which should be preferred, particularly, in the case of complicated systems, and which renders directly evident the connection of the thermodynamic theory with the theory of the after-effects of the relaxation phenomena.

We shall simplify our manner of notation to some extent, by designating the deviations from the state of reference by $\bar{v} = v - v_0$, $\bar{p} = p - p_0$, $\bar{s} = s - s_0$, $\bar{T} = T - T_0$.

It will then follow from [16] by integration of this differential equation in p , following some simple transformation, that

$$\begin{aligned} \bar{p}(t) = A e^{-t/\tau_{sv}} + \left(\frac{\partial p}{\partial s}\right)_{v, \xi} \cdot \bar{s}(t) + \left(\frac{\partial p}{\partial v}\right)_{s, \xi} \cdot \bar{v}(t) - \left(\frac{1}{\tau_{sv}} - \frac{1}{\tau_{pv}}\right) \left(\frac{\partial p}{\partial s}\right)_{v, \xi} \int_0^\infty \bar{s}(t-u) e^{-u/\tau_{sv}} du \\ - \left(\frac{1}{\tau_{sv}} - \frac{1}{\tau_{sp}}\right) \left(\frac{\partial p}{\partial v}\right)_{s, \xi} \int_0^\infty \bar{v}(t-u) e^{-u/\tau_{sv}} du \end{aligned} \quad [17]$$

When we conceive of [16] as a differential equation in v , we shall find analogously, by integration, that

$$\begin{aligned} \bar{v}(t) = B e^{-t/\tau_{sp}} + \left(\frac{\partial v}{\partial p}\right)_{s, \xi} \bar{p}(t) + \left(\frac{\partial v}{\partial s}\right)_{p, \xi} \bar{s}(t) + \left(\frac{1}{\tau_{pv}} - \frac{1}{\tau_{sp}}\right) \left(\frac{\partial v}{\partial s}\right)_{p, \xi} \int_0^\infty \bar{s}(t-u) e^{-u/\tau_{sp}} du \\ + \left(\frac{1}{\tau_{sv}} - \frac{1}{\tau_{sp}}\right) \left(\frac{\partial v}{\partial p}\right)_{s, \xi} \int_0^\infty \bar{p}(t-u) e^{-u/\tau_{sp}} du. \end{aligned} \quad [18]$$

Consequently, the instantaneous value of \bar{p} (or of \bar{v}) consists of a part that has been determined by the instantaneous values of \bar{v} and \bar{s} (or \bar{p} and \bar{s}) and of another part into which all earlier values of \bar{v} and \bar{s} (or of \bar{p} and \bar{s}) will go, with exponentially decreasing weights. This means that all earlier values of the two other variables present their after-effects in the instantaneous value of \bar{p} (or of \bar{v}). The term of the sum having the coefficient

A or B may be omitted. When we follow the system by starting from a state of equilibrium ($v = 0$, $\xi = \xi_0$ and $\bar{p} = 0$ for $t < 0$), then we shall find that $A = B = 0$; on the other hand, when the initial state is not a state of equilibrium, then it will not be necessary for A and B to disappear, but the term having the factor A or B will become negligibly small, after the lapse of a time of $\gg \tau_{sv}, \tau_{sp}$, and we shall always have to wait that long when we want to carry out meaningful measurements on the system.

The functions

$$\alpha_{s, n} \partial \left(\frac{\partial d_1}{\partial \xi_1} - \frac{\partial s_1}{\partial \xi_1} \right) = (n) \tau_{sv} \alpha_{s, n} \partial \left(\frac{\partial d_1}{\partial \xi_1} - \frac{\partial s_1}{\partial \xi_1} \right) = (n) \tau_{sp} \quad [19]$$

and

$$\beta_1(u) = \left(\frac{1}{\tau_{sv}} - \frac{1}{\tau_{sp}} \right) e^{-u/\tau_{sp}}, \quad \beta_2(u) = \left(\frac{1}{\tau_{pv}} - \frac{1}{\tau_{sp}} \right) e^{-u/\tau_{sp}} \quad [20]$$

are designated as after-effect functions of the pressure or volume in the case of changes of the volume and the entropy, or of the pressure and the entropy.

Analogous results will be obtained from [14].

4 Thermodynamic systems with a finite number of internal transformations.

We shall now consider a system with a finite number of internal transformations. We shall have them described by running reaction variables or by independent concentrations or by internal temperatures that have been defined in a suitable manner, or by other variables $\xi_1, \xi_2, \dots, \xi_n$. Let affinities of A_1, A_2, \dots, A_n that depend on s, v and the ξ_i 's be assigned to them, on the basis of the Gibbs's relation of $du = Tds - p dv - \sum_{i=1}^n A_i d\xi_i$. These affinities will disappear in the state of equilibrium. Then

$$\frac{d\xi_i}{dt} = \sum_{k=1}^n \epsilon_{ik} A_k \quad (i = 1, 2, \dots, n) \quad [22]^*$$

will be valid for the reaction velocities in the case of small deviations

* There is no Equation [21] in the German text. - Translator.

from the thermodynamic equilibrium, in accordance with the thermodynamics of the irreversible processes. In this equation, too, the ξ_{ik} 's may be considered to depend solely on the data of a reference state T_0, v_0 , near which the system will be assumed to be located. The reciprocity relations of Onsager, viz.,

$$\varepsilon_{ik} = \varepsilon_{ki} \quad (i, k = 1, 2, \dots, n) \quad [23]$$

will apply to them.

We shall now limit ourselves, inasmuch as nothing else will be stated expressly, to adiabatic changes of state, for which we shall be able to write $s = \text{const} = s_0$, within the same approximation within which (22) is valid. Then, there will be:

$$\frac{d\xi_i}{dt} = \sum_{l,k} \varepsilon_{ik} \left(\frac{\partial A_k}{\partial \xi_l} \right)_{v,s} (\xi_l - \xi_{l0}) + \sum_k \varepsilon_{ik} \left(\frac{\partial A_k}{\partial v} \right)_{\xi,s} (v - v_0), \quad (i = 1, 2, \dots, n). \quad [24]$$

It will now be convenient and possible to introduce n linearly independent linear combinations of the ξ_l 's and assigned affinities, in such a way that $(\partial A_k / \partial \xi_l)_{v,s}$ will be transformed into the unit tensor while ξ_{ik} will become diagonal (2). To this end, we shall have to suppose solely that $U(s_0, v_0, \xi_1)$ will have an absolute minimum for $\xi_1 = \xi_{10}$, and that all reactions will actually be completed.

Due to this transformation, the square form of the internal energy, in the case of constant $s = s_0, v = v_0$, for the new internal variables will be equal to one half of the sum of the squares of the new affinities, and the square form of the entropy generation will be reduced to a sum of the squares of the new affinities having positive coefficients. We shall now assume, here and in the following, that our ξ_l 's and A_l 's already have this property; then we shall have, in consequence thereof, in the case of constant $s = s_0, v = v_0$, - of course, near the state of equilibrium only -

$$u = \frac{1}{2} \sum_{i=1}^n A_i^2; \quad \frac{1}{T} \sum_{i=1}^n A_i \frac{d\xi_i}{dt} = \sum_{i=1}^n \frac{1}{T\tau_i} A_i^2.$$

This simultaneous transformation of two square forms on primary axes, will remind us of the corresponding transformation of the kinetic and potential energies of mechanical systems in the environs of a state of equilibrium, that leads directly to the normal oscillations and to their eigen-frequencies. But, the normal coordinates frequently do not have any importance of their own, on a mechanical system; rather, they are generally connected, in a quite complicated manner, with simple geometric data of the system. This applies altogether analogously to the internal "normal" variables of thermodynamic systems with relaxation. We should designate as simple internal variables those variables that are assigned to individual molecular mechanisms. Then, the normal variables will correspond to the usually rather complicated combinations of the individual mechanisms and each measured relaxation time will always be assigned to a normal variable and, thereby, generally not to one single molecule mechanism but to a certain combination of all mechanisms. The fact that the normal variables are generally different ones in the case of constant s, v than in that of constant s, p or T, v or T, p represents an additional complication.

On the basis of our assumption that the ξ_i 's are already normal variables, we shall arrive at the conclusion that, when

$$\varepsilon_{ik} = \frac{1}{\tau_i} \delta_{ik} \quad (\tau_i > 0, \delta_{ik} = 1 \text{ for } i = k, \delta_{ik} = 0 \text{ for } i \neq k)$$

$$\frac{d\xi_i}{dt} = -\frac{1}{\tau_i} (\xi_i - \xi_{i0}) + \frac{1}{\tau_i} \left(\frac{\partial A}{\partial v} \right)_{\xi, s} (v - v_0). \quad [25]$$

The totality of the τ_i 's is the relaxation spectrum (= totality of the relaxation times) for constant s 's and v 's as we can see immediately by the integration of [25] with $v \equiv v_0$. We shall now be able to eliminate the

$\xi_i - \xi_{i0}$ from [25] and from the equation of state as developed around the state of reference

$$s = s_0, v = v_0, \xi_i = \xi_{i0} = \bar{\xi}_i(s_0, v_0),$$

$$p - p_0 = \left(\frac{\partial p}{\partial v} \right)_{s, \xi} (v - v_0) + \sum_{i=1}^n \left(\frac{\partial p}{\partial \xi_i} \right)_{s, v} (\xi_i - \xi_{i0}) \quad [26]$$

and the dynamic equation of state as written formally, viz.

$$p - p_0 = \left\{ \left(\frac{\partial p}{\partial v} \right)_{s, \xi} + \sum_{i=1}^n \left(\frac{\partial p}{\partial \xi_i} \right)_{s, v} \left(\frac{\partial \xi_i}{\partial v} \right)_{s, A} \frac{1}{1 + \tau_i D} \right\} (v - v_0) \quad [27]$$

will come into existence.

D designates the differential operator d/dt . The real form will result from this formal version by means of multiplying away the denominators $1 + \tau_i D$. Consequently, [27] ties together the $p - p_0$, $v - v_0$ and the time derivations of these variables up to the r -th one, provided that the sum contained in [27] contains - possibly, by means of a summing up - exactly r terms with various τ_i 's.

Instead of [27], we shall write briefly

$$p - p_0 = \left(\frac{\partial p}{\partial v} \right)_{s, \xi} \cdot \left[1 - \sum_{i=1}^n \frac{\delta_i^2}{1 + \tau_i D} \right] (v - v_0), \quad [28]$$

when

$$\delta_i^2 = \left(\frac{\partial v}{\partial \xi_i} \right)_{s, p} \left(\frac{\partial \xi_i}{\partial v} \right)_{s, A}. \quad [29]$$

On the basis of the thermodynamic stability conditions, we shall arrive at the conclusion that

$$0 \leq \delta_i^2 \quad \text{and} \quad \sum_{i=1}^n \delta_i^2 < 1. \quad [30]$$

The relaxation times τ_i and the values of the coefficients δ_i evidently do not depend on our special choice of the internal variables, but the special representation [29] of the δ_i^2 's does, indeed.

In an analogous manner, we shall obtain

$$v - v_0 = \left(\frac{\partial v}{\partial p} \right)_{s, \tau} \left[1 + \sum_{i=1}^n \frac{\delta_i^2}{1 + \sigma_i D} \right] (p - p_0) \quad [31]$$

with non-negative δ_i^2 's, on the basis of the selection of p and ξ_i as independent variables. The σ_i 's are the adiabatic relaxation times in the case of constant pressure.

When all the τ_i 's are different from one another, and when all the δ_i^2 's are larger than 0, then the σ_i 's will also differ from one another, and all the δ_i^2 's will be larger than zero, and when all the τ_i 's and the σ_i 's have been arranged according to their size, then

$$\tau_1 < \sigma_1 < \tau_2 < \sigma_2 < \dots < \tau_n < \sigma_n. \quad [32]$$

will be valid.

The relaxation times τ_i , in the case of constant s, v , will therefore be separated from the relaxation times σ_i , in the case of constant s, p , in such a sense that the largest relaxation time τ_n of the first spectrum will be smaller than the largest one σ_n , of the second spectrum. To describe these conditions, we shall write briefly that

$$Sp(s, p) \nless Sp(s, v) \quad [33]$$

In an analogous manner, we shall be able to obtain the relations of

$$\begin{aligned} Sp(T, p) \nless Sp(T, v), Sp(T, v) \nless Sp(s, v), \\ Sp(T, p) \nless Sp(s, p). \end{aligned} \quad [34]$$

for the relaxation times in the case of other variables that are maintained constant. In [34], we have assumed that two relaxation spectra, that are connected by such a relation, do not have any multiple relaxation times, and that all the δ_i 's and τ_i 's, and all the values that correspond to them, in each case, in other spectra, differ from zero.

We shall now return once more to [28] and [31]. In the general case, neither all the τ_i 's will have to differ from one another, nor will all the δ_i 's have to differ from zero. But, then, it will always follow, from [28] and [31], by means of suitable summing-up, that

$$p - p_0 = \left(\frac{\partial p}{\partial v} \right)_{s, z} \left[1 - \sum_{i=1}^r \frac{\delta_i'^2}{1 + \tau_i D} \right] (v - v_0), \quad [35]$$

$$v - v_0 = \left(\frac{\partial v}{\partial p} \right)_{s, z} \left[1 + \sum_{i=1}^r \frac{\sigma_i'^2}{1 + \sigma_i D} \right] (p - p_0), \quad [36]$$

possibly with a different numbering of the τ_i 's and σ_i 's, and there will be $r \leq n$, $\delta_i \neq 0$, $\sigma_i \neq 0$. Under certain circumstances, the sum in [35], and thereby also the sum in [36] may be done away with, altogether. The τ_i 's or σ_i 's ($i = 1, 2, \dots, r$) are the relaxation times which show their effects in the thermodynamic equation of state. We call them the effective relaxation times, and we designate their totality as the effective relaxation spectrum Sp_e (s, v) or $Sp_e(s, p)$, when s, v or s, p are constant. When they are appropriately numbered, the equation

$$\tau_1 < \sigma_1 < \tau_2 < \sigma_2 < \dots < \tau_r < \sigma_r. \quad [37]$$

will apply to them, also. [37] follows directly from solving [35] for $v - v_0$ and comparing it with [36].

Analogous relations and statements will result when we keep the temperature constant, instead of the entropy. But in this case, the number of the effective relaxation times will not have to be equal to r . In the aforementioned example of the oscillation and rotation relaxation, the number of the isothermic effective relaxation times will be equal to zero, even when we consider all possibilities of transition, while the number of the adiabatic effective relaxation times will always differ from zero.

The integral form of $(p - p_0 = \bar{p}, v = v_0 - \bar{v})$ follows from the differential form [35] or [36] of the dynamic equation of state, by means of the identity that is valid for $\tau > 0$, viz.,

$$x(t) = (1 + \tau D) \int_0^{\infty} x(t-u) e^{-u/\tau} \frac{du}{\tau} \quad [38]$$

It is:

$$\dot{p}(t) = \left(\frac{\partial p}{\partial v} \right)_{s, \xi} \left[\bar{v}(t) - \int_0^{\infty} \bar{v}(t-u) \left(\sum_{i=1}^r \frac{\delta_i'^2}{\tau_i} e^{-u/\tau_i} \right) du \right], \quad [39]$$

$$\dot{v}(t) = \left(\frac{\partial v}{\partial p} \right)_{s, \xi} \left[\bar{p}(t) - \int_0^{\infty} \bar{p}(t-u) \left(\sum_{i=1}^r \frac{\sigma_i'^2}{\sigma_i} e^{-u/\sigma_i} \right) du \right]. \quad [40]$$

In these equations, the solutions of the homogeneous equation

$$(1 + \tau_1 D) \cdots (1 + \tau_r D) \bar{p}(t) = 0 \quad \text{or} \\ (1 + \sigma_1 D) \cdots (1 + \sigma_r D) \bar{v}(t) = 0.$$

have been omitted, for the reasons given above. For isothermic conditions, equations that are analogous to [39] and [40] will result.

In this way, we have obtained the formulation of the theory of after-effects; the adiabatic after-effect functions are:

$$\alpha(u) = \sum_{i=1}^r \frac{\delta_i'^2}{\tau_i} e^{-u/\tau_i}, \quad \beta(u) = \sum_{i=1}^r \frac{\sigma_i'^2}{\sigma_i} e^{-u/\sigma_i} \quad [41]$$

The σ_1 's, τ_1 's are determined unequivocally by the τ_1 's, δ_1 's, and vice versa.

We note expressly that several elementary relaxation processes (several molecular mechanisms) with equal relaxation times may be summarized in one effective relaxation process of the after-effect theory, but that - on the other hand - one elementary relaxation process (one molecular mechanism) will not necessarily have to become manifest in one effective relaxation process, and in addition, that one effective relaxation time may split under isothermic conditions into several effective relaxation times under adiabatic

conditions, or that it may not manifest itself at all, and vice versa.

All the considerations presented up to this point, and also many of the following ones can be translated almost literally for application to the case of di-electric relaxation; it will be necessary only to replace $p - p_0$ by the electric field intensity \mathcal{E} , and $v - v_0$ by the electric displacement density \mathcal{D} in order to obtain the description of the di-electric relaxation phenomena by means of the dynamic equation of state in its differential form (the dynamic enlargement of the static equation $\mathcal{D} = \epsilon \mathcal{E}$), or by the after-effect functions.

5. Relaxation spectra in systems having an infinite number of internal transformations.

We shall now attempt to transfer the results of the preceding Section to thermodynamic systems having an infinite number of internal variables ξ_i . It will be shown by an example in Section 7 that there are systems that may be conceived in this manner. In Section 8, we shall talk, by way of intimation, about the question as to the extent to which such systems may still be designated as thermodynamic systems.

For the sake of simplicity, we shall assume that the internal variables ξ_i form a discrete totality. Then, we shall immediately be able to take over all the results of the preceding Section inasmuch as no use is being made by them of the existence of normal variables. That applies directly only to equations [22] to [24], in which $i = 1, 2, \dots$, while the sums extend from $k = 1$ to ∞ . But, a more precise mathematical analysis, e.g., by means of the theory of infinite matrices or by the methods of the theory of integral equations, will show that, in addition, all results of the preceding Section, if they are interpreted correctly (which is indeed, obvious), will

remain essentially valid, inasmuch as they do not contain the normal variables in an explicit form. These are equations [28] and [30] to [41]. It will have to be kept in mind, however, that in the case of problems involving an infinite number of transformations, the relaxation spectra will not have to be discrete any longer but may be continuous or may contain continuous parts.

In that case, [39], [40], and [41] will be replaced by

$$\bar{p}(t) = \left(\frac{\bar{c}p}{\bar{c}v} \right)_{s, \bar{z}} \left[\bar{v}(t) - \int_0^{\infty} \bar{v}(t-u) \alpha(u) du \right], \quad [42]$$

$$\bar{v}(t) = \left(\frac{\bar{c}v}{\bar{c}p} \right)_{s, \bar{z}} \left[\bar{p}(t) + \int_0^{\infty} \bar{p}(t-u) \beta(u) du \right]. \quad [43]$$

The after-effect functions can now be written, generally, as Stieltjes-integrals with non-decreasing (cf. [30]) functions $\varphi(\lambda)$ and $\psi(\lambda)$:

$$\alpha(u) = \int_0^{\infty} e^{-\lambda u} d\varphi(\lambda), \quad \beta(u) = \int_0^{\infty} e^{-\lambda u} d\psi(\lambda) \quad (u \geq 0). \quad [44]$$

$\varphi(\lambda)$ and $\psi(\lambda)$ characterize the effective relaxation spectra in the case of constant s, v or s, p. Their points of discontinuity correspond to discrete relaxation times $1/\lambda$ while intervals of steady increase correspond to continuous parts of the relaxation spectrum. The after-effect functions are totally monotonous in $0 \leq u < \infty$, i.e., they can be differentiated there at will, and their n-th differential quotient ($n = 0, 1, 2, \dots$), differs from zero and has the sign of $(-1)^n$.

There exists a simple connection between the two spectra $\varphi(\lambda)$ and $\psi(\lambda)$. It may be obtained either by way of the Laplace transformation of equations [42] and [43] combined with the application of the folding theorem, or more directly, by presupposing that $\bar{v}(t)$ and thereby also $\bar{p}(t)$, is proportionate to $e^{i\omega t}$ with any (even a complex) ω , by inserting this into [42] and [43], as well as by entering $\alpha(u)$ and $\beta(u)$ from [44], and by integrating

for u . The result will be

$$\left\{1 - \int_0^{\infty} \frac{d\varphi(\lambda)}{\lambda + i\omega}\right\} \cdot \left\{1 + \int_0^{\infty} \frac{d\psi(\lambda)}{\lambda - i\omega}\right\} = 1. \quad [45]$$

This equation enables us to calculate, by a well-known method, $\psi(\lambda)$, provided that $\varphi(\lambda)$ is known, and vice versa (cf., e.g., (3), (4)).

When the effective relaxation spectrum $Sp_e(s, v)$ is discrete, then $\varphi(\lambda)$ will be constant, except for the points of discontinuity; this will then apply also to $\psi(\lambda)$ and $Sp_e(s, p)$ will also be discrete. The analogon of [37], viz.,

$$Sp_e(s, p) \not\approx Sp_e(s, v). \quad [46]$$

will then follow from [45]. It follows likewise that: When the $s\ddagger, v$ -spectrum also contains continuous parts, then the $s\ddagger, p$ -spectrum will contain continuous parts within the same areas. This statement is almost self-evident, when we conceive of the continuous system as a border-line case of a discrete spectrum with relaxation times that lie very closely together; for in that case, there will lie - according to a theorem of the preceding Section - between every two relaxation times of $Sp_e(s, v)$ a relaxation time of $Sp_e(s, p)$ and vice versa. But - and this is remarkable, indeed - that relaxation time of $Sp_e(s, v)$ which lies outside $Sp_e(s, p)$ does not, by any means, close off the continuous spectrum but is evident, outside that spectrum, as a discrete or isolated relaxation time.

We shall show this by an example, a continuous spectrum with constant occupation. Let us assume that $\varphi(\lambda) = 0$ for $0 \leq \lambda < a$, $\varphi(\lambda) = q(\lambda - a)$ that is for $a \leq \lambda \leq b$ and that $\varphi(\lambda) = q(b - a)$ for $\lambda > b$. Then, we shall have, when $i\omega = -z$

$$\int_0^{\infty} \frac{d\varphi(\lambda)}{\lambda - z} = \int_a^b \frac{q}{\lambda - z} d\lambda = q \ln \frac{b - z}{a - z} \quad [47]$$

and according to [45]

$$\int_0^{\infty} \frac{d\psi(\lambda)}{\lambda - z} = \frac{q \ln \frac{b-z}{a-z}}{1 - q \ln \frac{b-z}{a-z}}. \quad [48]$$

The integral [47] will be unequivocal and finite everywhere, provided we exclude a branch line along the continuous spectrum $a \leq z \leq b$ from the complex z -plane. The right side of [48] will also be unequivocal, provided we exclude a branch line $a \leq z \leq b$, but it will be finite only with the exception of the pole z_0 for which

$$\ln \frac{b-z_0}{a-z_0} \text{ or } z_0 = a - \frac{b}{1-q} \quad [49]$$

will apply. It lies outside the interval $a \leq z \leq b$. To it, a discontinuity of $\psi(\lambda)$ in the point z_0 and of the value of

$$0 < 1 - \{(b_{11} - 1)(1 - b_{11}^2)\} \frac{b}{b-q} = \frac{(v-q)b}{(vz-v)(vz-q)} = d \quad [50]$$

and an isolated relaxation time of $\frac{1}{z_0} > \frac{1}{a}$ outside the interval of $(\frac{1}{b}, \frac{1}{a})$ will correspond.

Otherwise, $\psi(\lambda)$ has growth points only within the interval of $a \leq \lambda \leq b$. They may be found by assuming on both the right and left sides of [48] that $z = \lambda + iy$ and by performing the passage to the limit $y \rightarrow 0$. It will then follow that

$$d\psi(\lambda) = \frac{q}{\pi^2 q^2 + \left[1 + q \ln \frac{b-\lambda}{\lambda-a}\right]^2} d\lambda, \quad [51]$$

Otherwise, i.e., for $0 \leq \lambda < z_0, z_0 < \lambda < a, b < \lambda < \infty$, $\psi(\lambda)$ will be constant in each case.

We shall summarize: The continuous spectrum $Sp_e(s, v)$ in $\frac{1}{b} \leq \lambda \leq \frac{1}{a}$ (without any isolated outside relaxation time) corresponds to a continuous spectrum

$Sp_e(s, p)$ within the same interval, with an additional isolated relaxation time above the interval.

6. The general linear theory of after-effects.

The thermodynamic theory of the relaxation phenomena led us, in the general case, to the dynamic equation of state [42] or [43] between $\bar{p}(t)$ and $\bar{v}(t)$, with totally monotonous after-effect functions of $\alpha(u)$ or $\beta(u)$. [42] and [43] are interdependent; both equations have the following characteristics:

1. They are linear and homogeneous; i.e., when $\bar{v}_1(t)$ leads to $\bar{p}_1(t)$, and when $\bar{v}_2(t)$ leads to $\bar{p}_2(t)$ then $\bar{v}_1(t) + \bar{v}_2(t)$ leads to $\bar{p}_1(t) + \bar{p}_2(t)$. This property is also called the superposition principle.

2. $\bar{p}(t)$ depends solely on $\bar{v}(t)$ and on the earlier values of $\bar{v}(t - u)$ when $u > 0$; analogously, $\bar{v}(t)$ depends only on $\bar{p}(t)$ and on the earlier values of $\bar{p}(t - u)$ when $u > 0$, i.e., $\bar{p}(t)$ is determined only by the earlier history but not by the future behavior of $\bar{v}(t)$ and vice versa. This property is also called the after-effect principle.

3. All points of the time axis are equivalent; i.e., when $\bar{v}(t)$ leads to $\bar{p}(t)$, then $\bar{v}(t + \Delta t)$ when Δt is randomly selected, will lead to $\bar{p}(t + \Delta t)$.

4. Limited $\bar{p}(t)$ corresponds to limited $\bar{v}(t)$, and vice versa.

These properties of systems having relaxation properties are so evident that one might attempt not to obtain them as inferences but to make them the basis of a relaxation theory for small deviations from the state of equilibrium. As a matter of fact, this approach is much older than the thermodynamic method and actually leads, despite the small number and the simple nature of the prerequisites to far-reaching conclusions.

First, it can be stated generally that a connection of the type of [42] or [43] exists between two functions $\bar{v}(t)$ and $\bar{p}(t)$ that comply with the four

abovementioned prerequisites provided that we shall allow non-proper functions (e.g., of the type of a Dirac δ -function) also as after-effect functions. Of course, the coefficient $\left(\frac{\partial p}{\partial v}\right)_{T,s}$ has by now largely been divested of its thermodynamic significance; it indicates simply which instantaneous pressure jump will occur when \bar{v} is changed suddenly, from the direction of the equilibrium. The index s will have to signify, however, that the process shall be adiabatic. In the case of an isothermic process, [42] and [43] would also be valid, but with another coefficient, viz., with

$$\left(\frac{\partial p}{\partial v}\right)_{T,p} \quad \text{and} \quad \left(\frac{\partial v}{\partial p}\right)_{T,p} \quad \text{respectively,}$$

and with other after-effect functions of $\alpha(u)$ and $\beta(u)$.

We do not wish to indicate all possible after-effect functions, but only to point out the various possibilities by means of a few characteristic examples.

1. The thermodynamic theory of the relaxation phenomena provides

$$\alpha(u) = \sum_{i=1}^{\infty} A_i e^{-u/\tau_i} \quad [52]$$

when $\sum A_i < \infty$ and $\sum A_i \tau_i < 1$, while A_i and τ_i are otherwise selected at random, as possible after-effect functions in [42]. Instead of the sum, a Stieljes-integral may be written, even more generally, in [52]. Then, the after-effect function $\beta(u)$ has been determined unequivocally; it will have the form of

$$\beta(u) = \sum_{i=1}^{\infty} B_i e^{-u/\sigma_i} \quad [53]$$

when B_i and σ_i are also positive.

2. A more general group of after-effect functions has also the form of [52] and [53], but with complex A_i 's and τ_i 's, or B_i 's, that will have to

satisfy certain other restrictions. It is necessary, among other things, that the real part $\frac{1}{\tau_i}$ of $\frac{1}{\tau_i} = \frac{1}{\tau_i} + i \omega_i$ is positive. It is sufficient, in any case, for A_i and τ_i to be positive, and for $\sum A_i$ to be larger than ∞ and for $\sum A_i \tau_i$ to be larger than 1. We shall omit the formulation of the necessary and sufficient conditions and shall limit ourselves to the case of two terms of the sum in [52] with a positive coefficient A and with conjugated complex values of $\frac{1}{\tau_i} = \frac{1}{\tau_0} \pm i \omega_0$, due to the reality of $\alpha(u)$. Then, we shall find that

$$\alpha(u) = 2A e^{-u/\tau_0} \cos \omega_0 u$$

when $0 < 2A\tau_0 < 1$. It follows from [42] for harmonic processes with the time dependency of $e^{i\omega t}$ that

$$p(t) = \left(\frac{\partial p}{\partial v} \right)_{v=0} \left[1 - \frac{A}{\frac{1}{\tau_0} + i(\omega + \omega_0)} - \frac{A}{\frac{1}{\tau_0} + i(\omega - \omega_0)} \right] v(t).$$

This, however, is a connection that is typical for systems with attenuated oscillation in the case of periodic excitation; ω_0 is the resonance frequency and τ_0 is reciprocal to the attenuation constant. On account of the resonance qualities of these systems, it is possible also to call them systems with resonance relaxation.

Systems of this type are covered by the so-called function-theoretical method in the linear after-effect theory (3). As examples thereof, we may indicate the behavior of dielectric media upon excitation with frequencies in the range of the visible light and of light with still shorter waves (optical absorption and dispersion - here, the electric displacement density takes the place of \bar{v} , and the electric field density takes the place of p —), but also finely distributed small gas bubbles in a liquid. These systems, and similar ones, are truly two-phase systems in which one phase is finely distributed

within the other one. The thermodynamics of the irreversible processes may be applied to it, provided we take into account the non-homogeneity of the system in an explicit manner. But, a concept of these systems looking upon them as genuinely homogeneous but with appropriate internal variables, is not possible within the framework of the thermodynamic relaxation theory. But, it seems that a thermodynamic relaxation theory may be developed by means of an extension of the thermodynamics of the irreversible processes. This theory will comprise also those systems that then will have to be considered macroscopically homogeneous; it will provide resonance relaxation and should enable us, due to its formalism, also to describe thermodynamically the behavior of the homogeneous dielectric matter for frequencies of visible light.

3. An additional group of after-effect functions contains non-proper functions. The simplest example is the function

$$\text{when } \alpha(u) = a \cdot \delta(u - T) \quad (T > 0, a < 1) \\ \delta(x) = 0 \quad \text{for } x \neq 0, \quad \int_{-\infty}^{\infty} \delta(x) dx = 1.$$

It follows hence, from [42] that

$$p(t) = \left(\frac{\partial p}{\partial v} \right)_{s, \xi} \left[\bar{v}(t) - a \bar{v}(t - T) \right].$$

By solving this equation for $\bar{v}(t)$, we shall find that

$$\bar{v}(t) = \left(\frac{\partial v}{\partial p} \right)_{s, \xi} \left[\bar{p}(t) + a \bar{p}(t - T) + a^2 \bar{p}(t - 2T) + a^3 \bar{p}(t - 3T) + \dots \right]$$

and thereby,

$$\beta(u) = a \delta(u - T) + a^2 \delta(u - 2T) + a^3 \delta(u - 3T) + \dots$$

Such a system has very curious properties. When the volume is changed suddenly, it will first present an instantaneous change of pressure and then, after the lapse of a time T , another sudden change of pressure; conversely,

a sudden change of the pressure would be followed by an instantaneous change of volume, and additional sudden changes of volume that would decrease by geometric progression, would follow after the lapses of the times of T , $2T$, and $3T$.

7. The problem of dielectric relaxation.

A simple example of the thermodynamic relaxation theory of a system having an infinite number of internal variables is a distribution of dipoles in a liquid. We shall assume, for the sake of simplicity, the case without a field, and presuppose that, at the time of $t = 0$, a random deviation from the equilibrium distribution is present. When $f(\vartheta, \varphi) \sin \vartheta d\vartheta d\varphi$ is the excess of the dipoles (assumed to be spherically symmetric), per unit of volume, the direction of which lies in the space angle of $\sin \vartheta d\vartheta d\varphi$, over the equilibrium value, then we shall find for the adjustment of the equilibrium distribution, according to Debye, that

$$\frac{\zeta}{kT} \frac{\partial f}{\partial t} = \sin \vartheta \frac{\partial}{\partial \vartheta} \left(\frac{1}{\sin \vartheta} \frac{\partial f}{\partial \vartheta} \right) + \frac{\partial^2 f}{\partial \varphi^2}$$

when ζ is a viscosity constant while k is the Boltzmann-constant. This equation agrees completely with equation [24], with $v = v_0$. This will become even more evident when we introduce a normal variable ξ_1, ξ_2, \dots . That is done by the transformation from $f(\vartheta, \varphi)$, to the ξ_1 's, in accordance with the development of the spherical function (we assume here, for the sake of simplicity, that the initial distribution does not depend on φ , viz.:

$$f = \sum_{n=1}^{\infty} \xi_n P_n(\cos \vartheta).$$

It follows then, on account of

$$\sin \vartheta \frac{\partial}{\partial \vartheta} \left(\frac{1}{\sin \vartheta} \frac{\partial}{\partial \vartheta} P_n(\cos \vartheta) \right) - n(n+1) P_n(\cos \vartheta) = 0$$

by comparing the coefficients, that

$$\frac{\zeta}{kT} \frac{\partial \xi_n}{\partial t} = -n(n+1) \xi_n (n=1, 2, \dots)$$

This system of equations agrees exactly with [25], with $v = v_0$. Consequently, each normal variable ξ_n has a pertinent relaxation time of $\tau_n = n(n+1)kT$. The total of these relaxation times constitutes the relaxation spectrum. Depending on the isothermic or adiabatic adjustment of the equilibrium, different values would have to be assigned to ζ . Experimentally, the adiabatic case should always be present.

The fact that only the slowest relaxation process will present the effect of $\tau_1 = 2kT$ in the electric moment is noteworthy, but clearly evident because of the properties of spherical functions; for, when we calculate the moment, then the integral

$$\int_0^\pi \cos \theta j(\theta) \sin \theta d\theta = \int_{-1}^1 u \cdot \sum_{n=1}^{\infty} \xi_n P_n(u) du = \frac{2}{3} \xi_1$$

is decisive. This means that the relaxation of the electric moment is conditioned solely by the relaxation of ξ_1 .

8. Linear kinetic theories as relaxation theories.

While the far-reaching consequences of the thermodynamic theory of the relaxation phenomena are already becoming evident from the example discussed in the preceding Section, they will be even more pronounced when we attempt - in a very successful manner - to conceive of the basic kinetic equations as relaxation equations. As a matter of fact, the basic kinetic equations for homogeneous systems with a distribution function of \hat{f} have the form of

$$\frac{\partial \hat{f}}{\partial t} = L\hat{f}. \quad [54]$$

Examples are Bloch's integral equation of the metal-electron theory and Boltzmann's fundamental equation of the kinetic gas theory. L is an operator and, in the kinetic gas theory, particularly, the collision integral. In the case of small deviations from the thermodynamic equilibrium, i.e., from the Fermi-distribution in the case of metal electrons, and from the Maxwell-distribution in gases, the operator L will be linear, in the first approximation.

Then, equation [54] will again agree with $v = v_0$ and it will be possible once more to introduce the normal coordinates ξ_1, ξ_2, \dots , by developing f for the eigen-functions of the equation $L f_n = -\lambda_n f_n$; we shall then find - when $f = \sum_i \xi_i f_i$ - by insertion into [54] and by comparison of the coefficients, that

$$\frac{d\xi_i}{dt} = -\lambda_i \xi_i.$$

The relaxation spectrum is defined by the reciprocal values of the λ_i 's. In addition, variations of external parameters - e.g., of the volume - can be covered - by way of analogy to (42) - by an additional linear term having $\bar{v}(t)$ as a factor in [54], and we shall finally find A, at least as a principle - it is another question whether this can also be realized in practice - a systematic procedure for the derivation of approximations for the fundamental equation as enlarged in this manner. It is largely based on the assumption that, in the case of variations of an external parameter, all relaxation times that are small in relation to the time during which noticeable changes occur, may be considered infinitely small in the first approximation. That means that we shall be able to write in the after-effect equation [42] which here, too, is valid, that

$$\begin{aligned} \int_0^\infty v(t-u) a(u) du &= \int_0^\infty v(t-u) \sum_{i=1}^\infty A_i e^{-u/\tau_i} du \\ &= v(t) \cdot \sum_{i=n+1}^\infty A_i \tau_i + \int_0^\infty v(t-u) \sum_{i=1}^n A_i e^{-u/\tau_i} du, \end{aligned}$$

provided that the relaxation times $\tau_{n+1}, \tau_{n+2}, \dots$ may be considered small in relation to the times during which the prescribed $\bar{v}(t)$ varies noticeably. Such systems, in which the rapid relaxation processes as such do not play any part, are called "aged" ["gealterte"] systems.

This concept of the kinetic theory as representing the most general examples of the thermodynamic theory of the relaxation phenomena causes this theory and the kinetic theories of the relaxation phenomena to merge. An

argument in favor of this concept is rendered possible by the full use of the concept of the fictitiously inhibited equilibrium as introduced by Schottky; this means that we shall be allowed, in our minds, to consider all transition probabilities between various argument values of the distribution function as inhibiting factors that are equal to zero. Then, however, we shall be able to use the methods of thermodynamics and to calculate - for such a system in a random state of non-equilibrium which, however, must not be too far removed from the equilibrium, the thermodynamic functions as dependent on the total of the values of the distribution function. The justification of this method may also be found in the fact that the oscillations that have been calculated on its basis by the thermodynamic oscillation theory, agree with the oscillations as calculated according to statistical mechanics.

9. Final remarks.

The formalism and the general laws of the thermodynamic relaxation theory may be considered sufficiently clarified. Two kinds of values enter into this theory. The values of the first type are the thermodynamic functions for the fictitiously inhibited equilibrium; they may be obtained from statistical mechanics and may be calculated for many examples. The values of the second type, the phenomenological coefficients ϵ_{ik} in [22], the transition probabilities between various argument values of the distribution function in [54], are of an incomparably more complicated nature and can be obtained only on the basis of difficult kinetic considerations that are largely of a quantum-mechanical nature. Despite many beginnings, almost everything still remains to be done in this field - no matter which type of relaxation phenomena is under discussion.

We were able only to hint at the possibility of a thermodynamic resonance relaxation. We hope that we shall be able to return to it at another occasion.

The same hope applies to the treatment of the fundamental kinetic equations in the sense of the relaxation theory; it would be interesting to find the relaxation spectra at least for one example, perhaps for a gas model with rigid and smooth spheres.

It is possible to develop - as a counterpart of the relaxation of pressure and volume as discussed above, and largely parallel to it - a theory of the elastic relaxation in isotropic or anisotropic bodies, and a theory of the dielectric and magnetic relaxation in anisotropic bodies. We shall soon discuss elsewhere the elastic bodies with thrust relaxation and pressure relaxation.

It must finally be pointed out that transfer phenomena also play a part in many relaxation phenomena. They have been examined thoroughly inasmuch as the acoustic relaxation is concerned (6).

Bibliography

- 1) Kronig, R. de L., Phys. Z. 39, 823 (1938).
- 2) Meixner, J. Z., Naturforschung 4a, 594-600 (1949).
- 3) Perron, O., Kettenbrueche (Leipzig and Berlin, 1929) 2. Edition.
- 4) Gross, B., Mathematical Structure of the Theories of Viscoelasticity (Paris 1953).
- 5) Hiedemann and Spence, Z. Phys. 133, 109-123 (1952), (there, additional references may be found).
- 6) Meixner, J. Acustica 2, 101-109, (1952).

Discussion

Moderator: S. Fluegge (Marburg/Lahn)

J. Meixner (Aachen): By way of conclusion of my report, I want to pose a few questions and touch upon a few problems the treatment of which, in my opinion, could be of interest for a further development of the theory as well as for the interpretation of experimental findings.

1. What simple examples illustrating the relaxation theory can be found?

2. Are there any systems having a so-called "dead time" such as has been discussed as the third example of the 6th Section of the Report.

3. Which data can be obtained, maximally, from a measured dispersion and absorption curve, in regard to the relaxation spectrum, provided that the value of the measuring errors can be estimated? This is a purely mathematical problem. Important contributions to this problem have already been made by Stavermann and Schwarzl; cf., in this respect, Mr. Staverman's paper.

4. The pertinent retardation spectra should be calculated for as many given relaxation spectra as possible. A first compilation of this type may already be found in B. Gross, Mathematical Structure of Theories of Linear Viscoelasticity (Paris 1953).

5. The relaxation properties - particularly the relaxation spectra - should be calculated for as many models as possible.

S. Fluegge (Marburg): I suggest that the following three complexes of problems be treated successively in the discussion:

First: To which extent are the ϵ_{ik} 's entropies, and to what extent are they not entropies? The second question would be: to what extent can your thermodynamic theory be applied to practical examples? Finally, the questions posed at the end of the Report, e.g., the resonance behavior, the significance of the concept of "dead time", will remain as the third question. We should, perhaps, adjourn mathematical questions until we shall discuss the paper by Gross.

H. B. G. Casimir (Eindhoven): When you discuss the relaxation phenomena with several variables, you introduce the values ϵ_{ik} . In that way, the formulae will have a particularly simple form, since the matrix as well as the matrix of the derivations $d A_k / d \xi_1$ has been diagonalized. This is based on

the fact that it is a symmetrical matrix, due to the Onsager relations. It is true, however, that the ϵ_{ik} 's will not have to be symmetrical, e.g., for a system within a magnetic field. It will then be true only that ϵ_{ik} will have to become ϵ_{ki} when the magnetic field is reversed. For that reason, the ϵ_{ik} -matrix cannot be diagonalized, and relaxation phenomena may result, accordingly, that are much more complicated and that will not fit into the general formalism.

J. Meixner (Aachen): Undoubtedly, the situation is more complicated in this case. But I believe that here, too, certain general statements can be achieved.

S. Fluegge (Marburg): To what extent can such a case occur, are there any additional examples?

H. B. G. Casimir (Eindhoven): I believe that, outside of magnetic fields, this case occurs only in systems that are in a state of rotation, e.g., in a system within a centrifuge, but this is already very artificial. But, actually, it may occur very well in a magnetic field.

J. Meixner (Aachen): In this respect, we could also say that the ϵ_{ik} 's are, as a matter of course, functions of state. But, in the environment of an equilibrium - and, in the linear theory, we are always within the environs of an equilibrium -, they depend solely on T, p and on the constant parameters of the system. As Onsager and Casimir have demonstrated, symmetry relations apply also to these ϵ_{ik} 's; there relations are, in these cases, particularly simple and allow of simple conclusions when there is no magnetic field present. They will become more complicated in the case of a magnetic field.

S. Fluegge (Marburg): Evidently, you presuppose - in view of the thermodynamic structure of your theory - homogeneous systems whenever you talk about

functions of state. To what extent is this supposition actually fulfilled by practical applications? I can imagine that you will have local heating or similar phenomena during the deformation so that these suppositions will be no longer valid?

J. Meixner (Aachen): In this respect, we can say the following: It is always true for the case of acoustic relaxation that we have heat conduction, simply because heating and cooling alternate as to time and place. Moreover, thrust deformations will occur in the acoustic wave, and the viscosity will also play a part. But, the considerations may be enlarged by including the transport phenomena explicitly in the equations.

S. Fluegge (Marburg): This means that the general frame will remain preserved, but you will obtain additional terms. It does not mean, however, that you will have additional non-linear terms instead of linear relations? Otherwise, the concept of relaxation time would, indeed, be also undermined!

J. Meixner (Aachen): No. I have intentionally restricted myself here to homogeneous systems so as not to complicate needlessly the presentation of my paper. Moreover, I would like to mention that the irreversible transfer phenomena can be covered by the same formalism which I have outlined for the internal transformations. It will only be necessary, to that end, to divide the system into sufficiently small - but not too small - volume elements and to introduce, besides the internal variables of the individual volume elements, perhaps, their temperature as an additional internal variable. - By the way, H. Eisenstein^{*)} has discussed the effect of heat conduction on the paramagnetic relaxation, a short time ago.

E. Hueckel (Marburg/Lahn): When we do not have any special problem, then we certainly shall not be able to say anything as to the deviations that will

^{*)} H. Eisenstein, Phys. Rev. 84, 548 (1951).

have to be considered as being too small for a certain case? I mean that we shall certainly not be able to indicate the range of validity of the linear equation a priori?

J. Meixner (Aachen): No, that is a question all by itself. And, e.g., in the case of chemical reactions, the allowable deviations from the equilibrium are relatively small for the linearized theory.

E. Hueckel (Marburg/Lahn): And in the case of chemical reactions that take place rapidly?

J. Meixner (Aachen): The reactions may have any velocity whatsoever.

E. Hueckel (Marburg/Lahn): I mean reactions, for which the deviations are large.

J. Meixner (Aachen): Then, linearity is not guaranteed any longer. It is possible, of course, to investigate experimentally in each case, to what extent the linear theory will apply, and it will then become apparent that their range of validity frequently is very large. That applies, e.g., to the relaxation in high polymers, but particularly to the transfer phenomena. E.g., the linear Fourier-equation applies to the heat conductance in gases, under normal conditions, at least up to temperature gradients of 10,000 degrees per cm.

W. Heywang (Karlsruhe): I would like to pose a question regarding the failure of the thermodynamic theory in the case of oscillation problems. Since it contains only differential equations of the first order, experimental results with oscillations are not covered. It is true that, within a modest framework, - i.e., by the simple addition of the corresponding terms of inertia - the theory may be enlarged, but I do not know to which extent we shall then depend on the assumed model. How shall we be able to include and understand

such a term of inertia within the framework of a consistent thermodynamic theory?

J. Meixner (Aachen): The idea of introducing terms of inertia is rather obvious, since the resonance behavior of the mechanical models of the relaxation with elastic springs and "dashpots" is brought about by mounting masses not only on the end of the model but also within the model itself. At this moment, I am not yet able to say how the free energy for a thermodynamic system with an analogous behavior is to be understood. But, it seems to me that it is already possible to say a few things about the formalism. The free energy will still contain the derivations ξ_i of the internal variables according to the time, and the affinities will have to be defined not by the derivations of the free energy according to the internal variables ξ_i , but by the variation derivations

$$A_i = -\frac{\partial f}{\partial \xi_i} + \frac{d}{dt} \frac{\partial f}{\partial \dot{\xi}_i}$$

It will then be possible - in a manner similar to Hamilton's mechanics - to assign canonically conjugated variables $\partial f / \partial \dot{\xi}_i$ to the internal variables ξ_i .

W. Heywang (Karlsruhe): To be more specific, I was concerned with a dielectric (ferro-electric) problem within a frequency range, in which a purely electrodynamic treatment that would be free of thermodynamics, still appeared to be unjustified, but in which, due to the special structure of the body under investigation, internal inductivities could occur within smaller ranges. I attempted, therefore, to fit the terms of inertia that described the inductivity, into the thermodynamics.

J. Meixner (Aachen): I believe - and this is, at the moment, no more than a profession of faith - that it will be possible, in the end, to generalize the thermodynamics of irreversible processes to such an extent that it will

cover this (the resonance case) also, but I am as yet unable to formulate this in any detail.

R. A. Sack (Liverpool): I have worked lately on this problem - it is true, not from the thermodynamic point of view but from the statistic-kinetic one. It appears that even in the case of the pure relaxation, when no oscillation is present, terms of inertia will have to be taken into account in certain cases. When we start - in doing so - from the Hamilton-function of the total system, then the ξ_1 's will be certain purposefully selected coordinates in the space of configuration which, together with other coordinates and with the canonically conjugated impulses enter into Liouville's equation, which describes the probability distribution in the phase space. Then, relaxation will mean transmission of energy from the partial system of the $(\xi_1, \bar{\xi}_1)$'s unto the remaining coordinates. But, the primary processes for such energy transmissions are not changes of location, i.e., variations of the ξ 's, but collisions, i.e., variations of the $\dot{\xi}$'s, and inasmuch as these are concerned, the inertia plays a principal part. For that reason, relaxation of the ξ 's will first require a new distribution of the velocities, the adjustment time of which shall be designated by τ^* . The common relaxation theories take only distributions of the ξ 's, and not of the $\dot{\xi}$'s into account, or they consider altogether only the statistical mean values of the ξ 's, and for that reason, they can be used only in the case of time lapses of $t \gg \tau^*$ or frequencies of $\omega \ll 1/\tau^*$. It results, particularly, from a proper consideration of the velocities that, when a field that has been kept constant for a long time is cut off suddenly, the tangent of the chronological curve of the course of all ξ 's will have to be horizontal at the first moment $t \ll \tau^*$, $t \rightarrow 0$, and that it will not fall as it is shown customarily. In an analogous way, it is also

true that, for alternating fields, Debye's Function $(1 + i\omega\tau)^{-1}$ fails in the case of frequencies, in which we have $\omega\tau \sim 1$; the failure consists in its predicating exaggerated losses; this has already pointed out by F. H. Mueller, among others *).

(Subsequently added: By way of summarizing my comments, I want to point out once more that the velocities $\dot{\epsilon}$ will, therefore, have to be considered not only in the case of oscillation phenomena, but also in a consistent calculation of the pure relaxation. I assume that this means that, in a thermodynamic treatment, the kinetic energy connected therewith will have to be taken into account explicitly).

F. H. Mueller (Marburg/Lahn): Perhaps, we should recall here, first of all Rocard's **) calculations. In Debye's classical paper on dipole dispersion (1913) just as in Einstein's calculations for the diffusion, the acceleration period for the movement of the dipoles has been neglected in favor of the time of the rotation in the field at a constant velocity, according to Stoke's equation of friction. The frequency dependence for ϵ' will then correspond no longer to the real part of the Debye function, but will read:

$$\epsilon'(\omega) = \epsilon_{\infty} + \frac{A\epsilon}{1 + \omega^2\tau^2} \cdot \frac{1 + J\omega^2 2kT}{1 + (J\omega 2\tau kT)^2}$$

Rocard complements the differential equation for the distribution function f by a term of inertia, viz.,

$$J \cdot \frac{d^2 \theta}{dt^2}$$

The frequency curve of $\epsilon'(\omega)$ is, therefore, somewhat changed in relation to the Debye function - not exactly, but into the direction of the transition to the resonance case. At the moment, I do not know whether this is due solely

*) Debye, P., Phys. Z. 35, 101 (1934); F. H. Mueller, Ergebnisse der exakten Naturwissenschaften 17, 181 (1938).

**) Rocard, M. J., J. Physique 4, 247 (1953).

to certain simplifications that are necessary to solve the differential equation for \dot{f} , viz., that the resonance case does not appear exactly. It has not yet been possible to confirm Rocard's theory. Even losses in dipole-free fluids such as benzene (V. D. H. Whiffen, Farad. Trans. 46, 124, 1950) require another explanation, in addition, even though one has attempted to use Rocard's calculations for that purpose.

B. Gross (Rio de Janeiro): A general after-effect theory that covers attenuated systems that are capable of oscillation, can be carried through. Only, such a theory is generally not called an after-effect theory any longer. E.g., the system theory of electric circuits can be reduced to a form that thoroughly agrees with the usual after-effect theory. I propose to make a few additional comments on this topic in my paper.

S. Fluegge (Marburg/Lahn): Mr. Sack, after all we have essentially to do with a generalization of Meixner's equation, in which you use an additional ξ . On the other hand, you will receive a very special statement concerning the horizontal tangent. Is this not, once more, a special model? In your case, it will probably always turn out that way, if you use the additional ξ 's. May I, Mr. Meixner, pose the additional question: this theory is here so much more special than the general formulation of the after-effect theory, and it particularly seems to result in the after-effect theory's always being monotonous?

J. Meixner (Aachen): Not only monotonous but totally-monotonous, i.e., the after-effect functions $\alpha(u)$, $\beta(u)$ and all their derivations for all u 's will differ from zero; more precisely, the first derivation will be negative, the second one will be positive, the third one will again be negative, etc., or also, that $\alpha(u)$, $\beta(u)$... may be represented as sums or integrals over

exponential functions $\alpha(\lambda)e^{-\lambda u}$, with positive $\alpha(\lambda)$ and λ 's.

S. Fluegge (Marburg/Lahn): Will this restriction, possibly, be nullified by Sack's objection? I.e., is it possible to describe, in addition, other processes, when we use the ξ 's in addition?

J. Meixner (Aachen): Yes, in that case, the after-effect functions will, of course, be different. But, when we exclude the small time interval during which the general theory happens to fail, without the ξ 's, then it will be a matter of course that equally totally-monotonous functions will result, within the framework of the thermodynamic relaxation theory. I am of the opinion that, when we make also use of Sack's theory, we shall, of course, obtain general after-effect functions that, however, will have to contain the totally-monotonous functions as a borderline case.

R. A. Sack (Liverpool): But necessarily only when the adjustment times of the Boltzmann distribution within the velocity space are much smaller than in the configuration space.

J. Meixner (Aachen): That will have to be presupposed.

H. B. G. Casimir (Eindhoven): In this connection, I may add that such a condition, viz., that one can select a time that is long in relation to the adjustment of the Boltzmann distribution and short in comparison to the time required, to achieve once more the state of equilibrium, that this is always an essential condition of such considerations. E.g., I have stressed in my derivation of the Onsager-equations that it happens to be possible only when such a time interval can be found, i.e., therefore, when this starting time is very short in relation to the relaxation times. On the other hand, I would like to ask, and this seems to me somewhat doubtful, whether it is possible outside the usual area, i.e., when the impulse adjustment time is

not sufficiently short, really to have confidence in a purely formal theory. I have the feeling that, in that case, the kinetic processes will become so complicated that it appears to be somewhat doubtful whether a general formalism will still do justice to this case. But, I have not seen Mr. Sack's papers, and it can be possible that it still can be done to a considerable extent. I just happened to have the impression that the thermodynamics just work out so beautifully, inclusive of the irreversible thermodynamics, because one just limits himself to the right area. It is very difficult to cover the phenomena by a still more general formalism.

J. Meixner (Aachen): But I believe that Mr. Sack knows better what's what, in this field. I do believe, however, that there will be a wider area within which we shall get along with this generalization, in which, therefore, the ξ 's are being used in addition, and we shall simply have to look for that area.

F. H. Mueller (Marburg/Lahn): I would like to address another question to Mr. Meixner, that is connected therewith: In an earlier paper^{*)}, he explained that, for a system in which transformations between the various components occur - be they of a chemical nature or between the numbers of electrons occupying the shell - any one of these concentrations is able to pass through "oscillating" states. Accordingly, the total effect will always disappear in a totally-monotonous manner, but not every individual component or number of electrons occupying the shell unconditionally for each representation (oscillating will have to be considered here to be not genuinely oscillating).

J. Meixner (Aachen): Yes, that is something entirely different from the resonance relaxation. Perhaps, I may say the following in this connection:

^{*)} J. Meixner, Z. Naturforschg. 4A, 594 (1949).

The choice of the internal variables is not unequivocal; for, when I have selected, e.g., the ξ_1 's as internal variables, then I may just as well take any independent linear combination of the internal variables as a new variable. The internal variables may be the numbers of occupying electrons, they may be the running reaction variables, but they may also be any combinations of the internal variables which I have just cited as examples. And it becomes evident that certain combinations which I call normal variables, in analogy to the normal coordinates of an oscillating mechanical system, that such internal variables altogether will adjust exponentially to the equilibrium value. As to a linear combination of the normal variables - the internal variables adapted to the problem in a natural manner, such as occupation figures, etc., are generally non-trivial combinations of the normal variables - it may happen that it adjusts to the equilibrium value in an oscillating manner. The word "oscillating" is here not strictly correct, because the number of the zero passages is finite; actually, it is - under adiabatic conditions - smaller by at least one, than the number of the independent internal variables.

S. Fluegge (Marburg/Lahn): That comes actually about in consequence of the fact that the negative sign is dominant in your linear combinations.

J. Meixner (Aachen): I.e., if we had $\xi_1 = \exp. (-\lambda_1 t)$, and $\xi_2 = \exp. (-\lambda_2 t)$, and if I now form a new internal variable $\xi_1 - \xi_2$, then a zero passage may occur for it. In this sense, a chemical equilibrium will not have to occur in a certain direction, but it may go beyond the goal and reach the equilibrium from behind; that is possible a finite number of times.

S. Fluegge (Marburg/Lahn): Could that contribute to the understanding of Liesegang's rings?

J. Meixner (Aachen): That, I don't know; I have never given it any thought.

M. Magat (Paris): I wanted to ask Mr. Meixner up to which frequency range the thermodynamic theory of the irreversible processes may be applied. I am interested in the converse case, in which the oscillations are excited by the electrons, while the translation energies and the rotation energies are limping behind, e.g., in the case of electric discharges (plasma oscillations, or similar phenomena).

J. Meixner (Aachen): Here, difficulties exist inasmuch as the temperature within the plasma is not unequivocally defined. It is necessary to differentiate between ion temperature, gas temperature, and electron temperature, and as far as I know, the ion temperature is not defined even by an unobjectionable Maxwell distribution.

M. Magat (Paris): That is exactly the problem. I shall formulate my question as follows: Let us assume that I know the excitation functions, the number of the electrons, and their velocities. To express it differently: I know the "temperature" of the electron excitation and of the oscillations. This temperature is transferred, with a certain relaxation time, unto the rotation and translation movement of the atoms and ions, by collisions. Will it then be possible, by means of your theory, to make any statements relating to the translation and rotation temperatures (or temperature since, as a matter of fact, both of them equate easily)?

J. Meixner (Aachen): I am unable to give you a definite reply to this question, just because of the aforementioned difficulties; it would have to be tried.

P. Brauer (Mosbach and Karlsruhe): I wanted to ask Mr. Meixner whether - if I have understood correctly - every after-effect can be reduced to a sum of e-functions. As a matter of fact, the reduction to e-function does not

provide any exact statement as to the elementary process. I am thinking just now, e.g., of an optical example, in which the ξ_1 's during the electron reactions are either the numbers of electrons occupying the shell or concentrations. It will then occur very frequently that reactions of a higher order will also be involved. Now then to what extent will it be possible, first, mathematically to replace such a fading function, in the presence of elementary reactions of a higher order, by a sum of e-functions, and to which extent will it be possible, if such a mathematical representation should be undertaken successfully, to establish a connection between the two "Fourier-systems"?

J. Meixner (Aachen): Between which two Fourier systems?

B. Brauer (Mosbach and Karlsruhe): Between the decomposition into e-functions and the decomposition into functions that are physically reasonable in relation to the process. Let us assume, e.g., that the ξ_1 -concentrations are present in a system with reactions of a higher order, and that one has relaxation phenomena, i.e., adjustment processes which also take place as reactions of a higher order. To what extent can a transition be made, in this case, between a linear theory that consists of a random number of artificial mathematical components, and the physically reasonable theory, which we shall then relate to the system of the physically well-known elementary processes that are not of the first order. To what extent is this possible, and what does it look like for simple cases?

S. Fluegge (Marburg/Lahn): Is this a physical or a mathematical question?

P. Brauer (Mosbach and Karlsruhe): Both.

J. Meixner (Aachen): I do not know to what extent I have understood your question correctly, but when I have a reaction of a higher order, and when it takes place near the state of equilibrium, then the theory will apply. When

we are not near the equilibrium then the theory will, of course, not be valid. It will then be very difficult to come to any sensible statements. E.g., when we find a random fading function, that reaches from a very large distance into the equilibrium, and when this function is reduced to e-functions, which - as a matter of principle - can be done mathematically, then I do not believe that any physical statement will be contained therein.

P. Brauer (Mosbach and Karlsruhe): I wanted to ask here a special question: when we are very close to an equilibrium, in the case of processes or elementary processes that are non-linear, as is, e.g., the concentration dependence in chemical reactions of a higher order, then certain functional connections will result, e.g., the velocity function, which will remain non-linear in a strict mathematical sense, even when we approach the equilibrium in a random manner.

J. Meixner (Aachen): Yes.

P. Brauer (Mosbach and Karlsruhe): Inasmuch as this case is concerned, I should be interested what else will then be predictable, possibly on the basis of the concentration dependence of the velocity function?

J. Meixner (Aachen): If you do not happen to have pathological cases, then the linear theory will always apply within the environs of the equilibrium, and it will then make no difference whether the reaction is one of the first order or of a higher order, in the meaning of the chemical terminology, whether it is mono-molecular or bi-molecular, etc. Mathematically, it will, of course, always be possible to construct pathological cases, but I can imagine a failure of the linear theory in the environment of the equilibrium only, when either, in the development of the free energy for the $\xi_1 - \xi_{10}$, the terms of the second order are lacking, and when, in accordance therewith,

the affinities are independent of the $\xi_1 - \xi_{10}$ in the first approximation, or when the phenomenological coefficients disappear in the first approximation, i.e., when the ξ_1 's are linear functions of higher potencies than the first one and of products of the affinities. But, I do not know whether there are any such cases.

S. Fluegge (Marburg/Lahn): How is the situation in the case of chemical reactions, in which you will, indeed, have noticeable changes in the concentration? How does a linearization look there?

J. Meixner (Aachen): This is, of course, only possible within the environment of the equilibrium, with the restrictions that I have just mentioned.

A. J. Staverman (Delft): When Mr. Brauer thinks that chemical reactions of a higher order will lead to non-linear processes, even when they take place near the equilibrium, then I believe that there exists a misunderstanding. It is true that, in that case, the reaction velocity is equal to the product of several concentrations, but when we write the concentrations - in the environs of the equilibrium - as a sum of equilibrium concentrations and a small additional term, then the product will nevertheless be - provided that we disregard the product of the additional terms - a sum of terms that are linear in relation to the additional terms.

G. Laukien (Stuttgart): The paper has ended with a question: Where will complicated forms of the curve occur? I want to point out that this is true of nuclear-magneton relaxations, as soon as they are examined by impulse methods. It will probably be more appropriate to present more detailed comments following Mr. Krueger's paper.

S. Fluegge (Marburg/Lahn): What about Mr. Meixner's question relating to "dead time"?

J. Meixner (Aachen): I have heard this catch-word only once but no details beyond it. But, I would be very much interested to hear examples. Once, when I talked to Mr. Feldtkeller, he gave a double-conductor as an example. When we apply a tension on the end of a double-conductor, then it will return from the other end only after a certain lapse of time; this phenomenon repeats itself at equal time intervals.

R. Feldtkeller (Stuttgart): Of course, that is not a true relaxation phenomenon.

J. Meixner (Aachen): But, it is nevertheless an example of the problem of "dead time"; for, this problem belongs, as a circuit problem, into the field of the after-effect theory and is a linear phenomenon.

E. Vogt (Marburg/Lahn): I want to ask whether the ferro-magnetic resonance that occurs at very high frequencies, when the ω_0 is determined by the Larmor frequency and when the form of the curve of resonance depends, as far as I know, on the energy transmission, may be considered an example for the resonance relaxation as described by Mr. Meixner. In that case, the curve is measured not by the variation of the frequency but by the variation of the magnetic field. Here, we find also a relaxation time, and I want to ask whether this is an example? (This would be an example that would be analogous to the case of nuclear resonance, as discussed in Krueger's paper).

J. Meixner (Aachen): At the moment, I am unable to tell you this.

H. Kneser (Stuttgart): What does an absorption curve or attenuation curve as a function of the frequency for the case of the "resonance relaxation" look like? Certainly, essentially like an ordinary resonance curve with considerable attenuation?

J. Meixner (Aachen): Yes.

F. H. Mueller (Marburg/Lahn): (subsequently): In the case of considerable attenuation, the difference from the case of a normal dispersion is, as a matter of fact, very small. When we plot the reduced attenuation against

$$\ln \omega/\omega_0 = \ln \omega \cdot \tau \left(\frac{1}{\tau} = \omega_0 = \text{frequency of the maximum} \right)$$

then it will become apparent that the curves of the resonance case are steeper than the ones of the case of a single relaxation time, according to the Debye-function (Fig. 1). As the attenuation decreases, the curves become more and more pointed and higher and higher. Analogously, the monotonous downward curve of the real part will become a serpentine line, such as it is known as typical for the curve of the refractive index over a resonance point. In the case of indistinct resonance around a point of gravity of an eigen-frequency, the resonance character can be recognized with certainty only by the real part; the bell-shaped curve of the attenuation may be just as flat or flatter than the Debye-function indicates. But, a steeper curve for anomalous absorption would also have to occur in Sack's case.

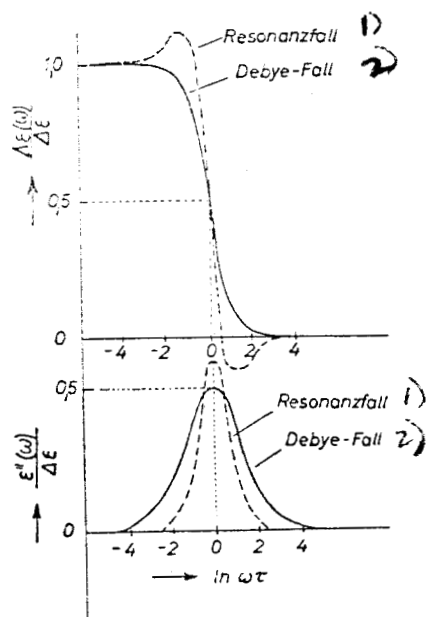


Fig. 1. Typical curve of the reduced real and imaginary part, with relaxation times for pure relaxation and for resonance relaxation.
1) Resonance case; 2) Debye's case.

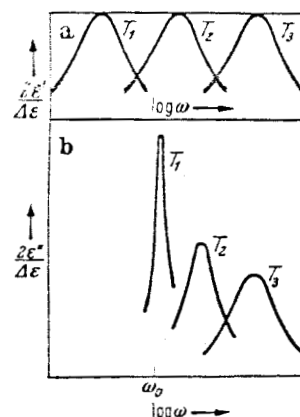


Fig. 2. Variation of the imaginary part with the temperature:
a) Debye's case; b) resonance case.

There is, by the way, an essential difference from the resonance case and from anomalous dispersion inasmuch as the behavior of the temperature is concerned, even though the outline drawn by Froehlich^{*)} (Fig. 2) represents an ideal borderline case. In high polymers, where the dispersion is certainly always anomalous, the increase as well as the decrease of the maximum occurs when the frequency increases. An explanation is not yet available. In the dielectric case, suggestions of resonance in dipole dispersion have always turned out to be simulated effects of the apparatus, up to this time. (Inductivities of the condenser feed lines had not been taken into consideration, etc.).

E. Jenckel (Aachen): In formula [10] on page 4 of your paper, you write a theorem of inequalities and you also expressly admit the equality. Do I understand this correctly, viz., that relaxation spectrum and retardation spectrum will become identical in the case of equality? Under what conditions are the two spectra equal? Kuhn has used certain experimental findings and has derived a distribution of such a type that relaxation phenomena and retardation phenomena will become equal. In my opinion, that would lead here to the result that the signs of equality will apply to your theorem. This relation is by no means always valid, but still applies to a sufficient number of cases, very roughly to some 50% of them. It would, therefore, be possible to use the case of equality as a base that occurs sufficiently often, and to consider the other cases by asking the question: what does the inequality mean, and what shall I have to add to the formulae so as to obtain the inequality?

^{*)} Theory of Dielectrics (Oxford 1949), page 103.

J. Meixner (Aachen): In this connection, we shall have to say that the distribution of the relaxation times and retardation times for a continuous relaxation spectrum in a finite interval of $0 < \tau \leq \tau_1$ will always be identical, with the exception of the isolated retardation time which will, then, occur of necessity in the retardation spectrum. But, it will be necessary to indicate, in regard to each relaxation time or to each retardation time, how strong its effect is, i.e., which are the coefficients of the development of the pertinent after-effect function for exponential functions. In this more complete sense, equality of relaxation and retardation would mean equality of the after-effect functions, and this exists, if an aftereffect exists at all, only then - and even then, only approximately - when the aftereffect is sufficiently weak. But, Mr. Gross will be able to express this very much better than I.

R. Gross (Rio de Janeiro): Relaxation spectrum and retardation spectrum will never be strictly identical, mathematically (even when we apply Kuhn's equation). But they will become more and more similar as the relaxing part decreases in relation to the purely elastic one.

F. Schwarzl (Delft): I may be able to answer Mr. Jenckels question. In reality, it is never possible to determine the spectra experimentally with sufficient precision, but only certain approximations. Consequently, even when the strict relaxation spectrum is different from the strict retardation spectrum, it may occur, nevertheless, that the approximations for the two spectra in the first order will be equal. In this case, the equality has less of a physical significance, but is simply an expression of the fact that it is not possible to determine the spectra experimentally with sufficient precision.

E. Jenckel (Aachen): That is possible, but there exist, experimentally, a considerable number of cases in which the spectra are clearly different.

R. Feldtkeller (stuttgart): It is possible to say in a very general way that the relaxation spectrum and the retardation spectrum are equal, to a reasonable degree of precision, when the unrelaxed elongation and the relaxed elongation differ but slightly.

E. Jenckel (Aachen): That agrees also quite thoroughly with the experimental experience.